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Controlled assembly of copper phthalocyanine with 1-iodooctadecane

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Abstract The binary assembly behavior of 1-iodooctadecane with substituted phthalocyanine (Pc) is studied using the scanning tunneling microscopy (STM). By altering the substituted alkyl groups attached to the phthalocyanine ring, either uniform assembly or phase separation behavior can be observed. It is suggested that the strength of intermolecular interaction between phthalocyanine molecules is the determining factor for the assembly structure.

Keywords: phthalocyanine, scanning tunneling microscopy, controlled assembly.

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Constructing of molecular nanostructure has generated great interest in the past decade, and the understanding of principles governing the assembling process is helpful to exploring viable routes of molecular engineering. For the self-assembly processes, the involved interactions are mainly intermolecular interactions of noncovalent types. The interactions in this category include electrostatic, van der Waals, hydrogen bonding, hydrophobic interactions, etc.[1].

The assemblies of single component systems, such as alkanethiols, have been studied rather thorough[8—11], while the 2-D assembly process of multi-component systems is not analyzed systematically, as compared to 3-D structures, in which much understanding has been accumulated. For the multi-component 2D assembly systems, the molecular assemblies could result in quite different results[12,13]. Whereas there exist several two-component assembly systems in which uniform assembly structures have been detected on the surface of substrate[14], the hydrogen bonding is attributed as the driving force. Little attempt has been seen on achieving molecular nanostructures on air/substrate interface based dominantly on van der Waals or electrostatic interactions possibly due to the lack of selectivity and directionality for these interactions. However, a number of reports are known in the literature to use inert spacer molecules, for example fatty acids or aliphatic amines, to separate or “dissolve” the molecules of interest in Langmuir-Blodgett films as well as in self-assembled films[15—17]. By adoption of this strategy, the orientation of -porphyrin ring can change from 40° to nearly parallel to the air/solution interface[16]. Such separation is of general interest when clusters or biologically active units are bound to surfaces. Well ordered assembly of nanometer TiO_2, PbS and other types of particles have been obtained using this method[17].

In the two-dimensional assembly system on substrate, the surface structure and properties could be substantial in the assembly characteristics. Due to the adsorbate-substrate interaction, surface bound 2D system could significantly differ with respect to that in the bulk crystal. A fine instance can be seen in the adsorption of 5-alkoxy- isophthalic acid, which has more compact arrangement in the 2D structure than in the bulk crystal and the way of hydrogen bonding is also different[14]. In this work we will show that with the binary mixture of 1-iodooctadecane (noted as C18I) and Pc, single molecular arrays of Pc can be formed. By altering the substituted alkyl groups attached to the Pc ring, either single molecular arrays or phase separation domains can be observed.

In our study, the polar groups of 1-iodooctadecane are arranged in an ordered manner between lamellae. It is noticed that these binary systems could provid a rich range of molecular interaction associated with functional groups. In this work we will show that copper phthalocyanine (later referred to as CuPc) and copper (Ⅱ) 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine (later noted as CuPcBU8) form single molecular arrays assembled by lamellae of C18I, while for copper (Ⅱ) 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H, 31H-phthalocyanine (noted as CuPcOC8), phase separation occurs.

1 Experiment

C18I, CuPc, CuPcBU8 and CuPcOC8 are all purchased from Acros and used without further purification. The solvent used in the experiments is toluene (HPLC grade, Acros) and the concentrations of all the solutions used are less than 1 mmol/L. Samples were prepared by dipping a drop of the above solution on freshly cleaved HOPG. Experiments were performed on a Nanoscope IIIA system (Digital Instrument Co.) operating in ambient conditions.

2 Results and discussion

Repeated STM studies reveal that the codepositions of 1-iodooctadecane with CuPc and CuPcBU8 result in uniform molecular assembly on the graphite surface. These assemblies are formed by intercalation of single Pc molecular arrays with C18I lamellae, which is a phase that has not been observed before. As shown in Fig. 1, these assembly domains can extend for hundreds of nanometers in size on the surface. In these images, the bright lines correspond to CuPc arrays while the relatively dark bands correspond to the C18I lamellae.

High-resolution STM images have been successfully obtained on these assemblies, as shown in Fig. 2(a) and (b), sub-molecular details of Pc can be seen on these im-

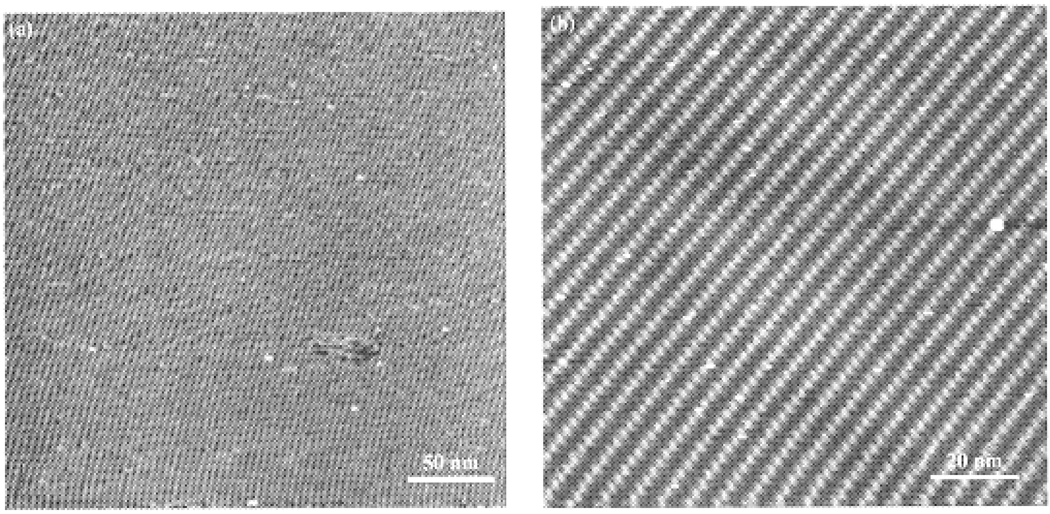

Fig. 1. Large-scale view of the uniform assembly formed by C18I with CuPc (a) and CuPcBU8 (b).

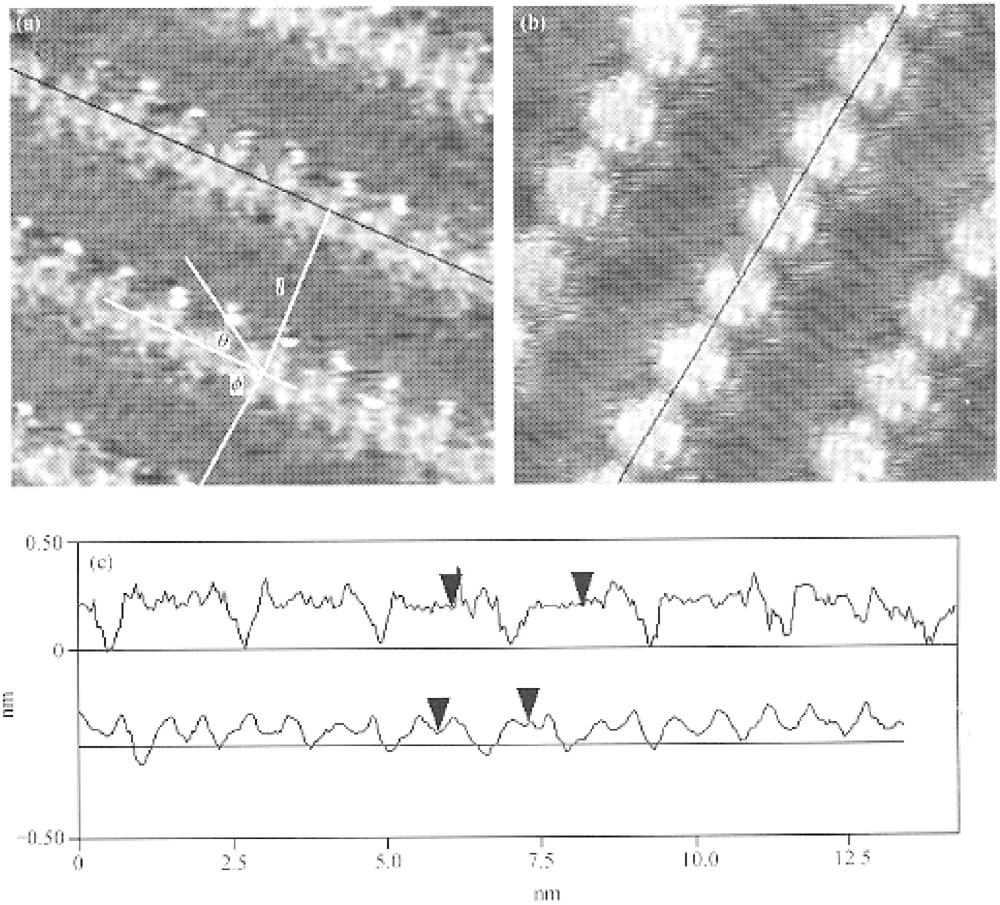

Fig. 2. High-resolution STM images obtained on the assembly structure of C18I with CuPc (a) and CuPcBU8 (b). (c) The section profile of the above images, showing the interval of Pcs in the molecular array.

ages and the carbon backbone of C18I molecules can also be seen. From Fig. 2(a), it can be measured that CuPcs tilt for an angle of 28±6° from the molecular array axis, this angle is defined as q in Fig. 2(a) and the angle between the orientation of C18I alkane chain and lamella axis is defined as f and the repeating period as l. In the one-dimensional molecular wire, CuPc molecules close packed with each other with its benzo groups fitting into the voids of the adjacent CuPc molecule, the same as in the close packed 2D CuPc monolayer. In the C18I lamellae, C18I adsorb with its carbon skeleton parallel to the surface and nearly perpendicular to the lamellae axis (f = 82 ± 4°). The measured width of CuPc molecular array is (1.50 ± 0.05) nm, while the width of the C18I lamellae is (2.50 ± 0.05) nm, in accordance with the molecular width of a planar adsorbed CuPc and the molecular length of C18I, respectively. In the case of CuPcBU8, the molecular width measured from the STM image is (1.84 ± 0.05) nm, while the repeating period l is (4.27 ± 0.05) nm. In the Pc molecular arrays, the distance between two adjacent Pc molecules, $d_{\text{Pc-Pc}}$ is (1.45 ± 0.05) nm for CuPc while for CuPcBU8 this value is (1.72 ± 0.05) nm.

Since tip-induced changes in the film structure are known to be relevant in some examples of scanning probe microscopy, this possibility should be considered and excluded for the present system. For this goal, control experiments were performed in which the tip was first engaged in a small scanning area, for example 20 nm × 20 nm, and after a uniform assembly was observed, the scanning area was enlarged abruptly to 200 nm × 200 nm. This test is based on the assumption that if the assembly structure of Pc with C18I is induced by tip, we would observe a 20 nm × 20 nm uniform assembly in the center which is surrounded by phase separation or disordered assemblies when the scanning area was enlarged. In fact, the observed image was completely uniform assembly within the scan area. This can serve as evidence that the observed assembly is not a tip induced change in the film structure. It should be noted that since the possibility that the tip induced transition is faster than the scanning speed is very small, this precaution test is reliable in most cases.

It can be estimated from the STM images that the molar ratio of Pc to C18I is 1∶3 in the case of CuPc, while for CuPcBU8, this value is 1∶4. This is consistent with the relatively large distance between CuPcBU8 molecules in the molecular array. In the assembly with CuPcBU8, the carbon skeleton of C18I orientated with an angle of f= 81 ± 4° with respect to the CuPcBU8 molecular array. Previous reports have shown that the carbon chain width in the close packed lamella is 0.45 nm, so the 1∶4 molar ratio is consistent with the molecular width of CuPcBU8 and carbon chain considering the orientation of the carbon chain.

Fig. 4 presents an image in which graphite lattices is shown simultaneously with the assembly of CuPcBU8/C18I, the azimuthal angle of the assembly with respect to the substrate can be determined from this image. The image clearly shows that C18I adsorb with registry to the substrate along the chain direction. From this image the azimuthal angle is estimated to be 7.6°[18] and the inter-CuPcBU8 distance is estimated to be 1.72 nm after correction of distortion using standard lattice parameters of graphite (0.25 nm). Similarly, the azimuthal angle of CuPc/C18I is determined to be 30°.

Proposed molecular models of these assemblies are shown in Fig. 3. In the case of CuPcBU8, because of the existence of butyl groups, the conjugated porphyrin ring is not accessible for the end groups of C18I molecules, this could be the reason for the larger repeating period (l) of the assembly of CuPcBU8/C18I compared with that of CuPc/C18I (Table 1). Considering the altering molar ratio of Pc/C18I and that the porphyrin ring is inaccessible for iodine in the case of CuPcBU8, it could imply that the interaction between the Pc and C18I molecules are mainly van der Waals. However it should be noted that the sites of Pc molecules accessible for C18I, in the case that CuPc is the benzo groups while for CuPcBU8 is the butoxy, have different polarizabilities and ionization potential, and hence could contribute differently to the van der Waals interaction. In addition, considering the redox activities of phthalocyanines and the iodine atom, partial charge transfer could also possibly have contribution to the interaction. As illustrated in a previous report in the charge transfer complex of phthalocyanine with Ⅰ, phthalocyanine do

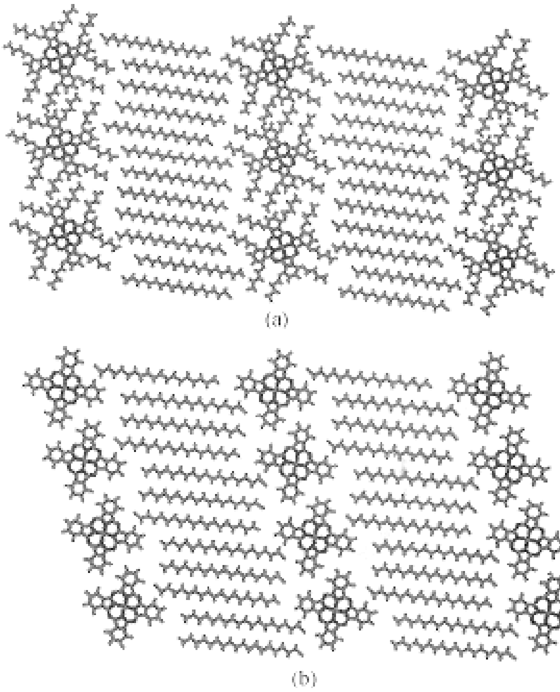

Fig. 3. (a) and (b) show the simulated molecular models representing the assembly structures of CuPcBU8 and CuPc with C18I.

Table 1 Parameters measured from the STM images of the uniform assembly of Pc with C18I

	CuPc/$C_{18}H_{37}I$	CuPcBU8/$C_{18}H_{37}I$
l/nm	4.06±0.05	4.27±0.05
q/(°)	28±6	26±5
f/(°)	82±4	81±4
Azimuthal angle/(°)	30	7.6
$d_{Pc\text{-}Pc}$/nm	1.45±0.05	1.72±0.05
Pc/C18I ratio	1∶3	1∶4

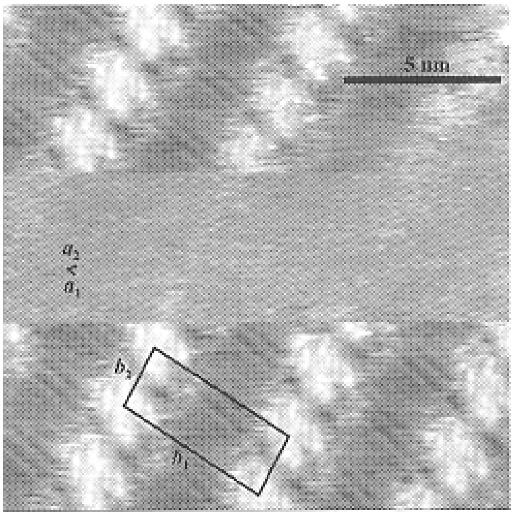

Fig. 4. STM image shows the assembly of CuPcBU8/C18I and underneath graphite lattice simultaneously. The unit cell of the graphite lattice is shown simultaneously with the unit cell of the assembly structure of CuPcBU8/C18I.

partially oxidized by iodine[21].

When C18I coadsorb with CuPcOC8 on the surface of HOPG, the phase separation behavior is frequently observed, with any presence of the above described uniform assembly. A molecularly sharp domain boundary is shown in Fig. 5. C18I arranged with iodine atoms paired together and carbon chains parallel to the graphite surface, while perpendicular to the lamellae normal. For CuPcOC8, arrangement with either four-fold or three-fold symmetry with its alkyl chains close packed together as previously reported were observed to coexist on the surface[22]. The four-fold symmetry is an indication of relatively weak molecule-substrate interaction, while considering that it is well established that alkanes will align with the substrate registry in their stabilized assemblies, the observed three-fold symmetry is reasonal. The coexistence of these two arrangements indicates they have approximately equal thermostability. Quantitative understanding of the polymorph of CuPcOC8 will require further experimental and theoretical studies. A molecular model of the four-fold structure is given in Fig. 6(d).

The adsorption structure of CuPc on graphite has already been reported[19,20]. Fig. 6 shows the arrangement of CuPcBU8 in a closely packed domain, with the molecular

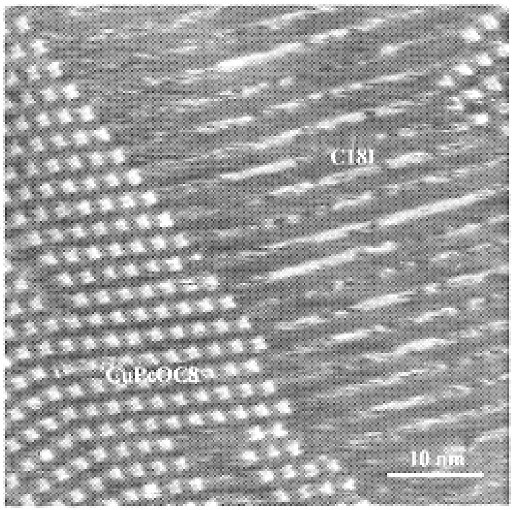

Fig. 5. Molecularly sharp boundary between domains of CuPcOC8 and C18I.

models schematically representing the arrangement of-CuPcBU8 shown in Fig. 6(c). In the close packed domain of CuPcBU8 there exist clearly two different orientations, with each tilt for about 45° from another. This is different from that of unsubstituted CuPc (shown schematically in Fig. 5(b)). In the assembly of CuPcBU8, the interval of CuPcBU8 is relatively smaller than expected from the assembly with butoxy fully extended. The butoxy groups are not detected in the current study. This may imply that the conformation of butoxy groups is not all-trans and it arranged randomly in the 2D crystal, bending out of the surface may also exist. Though in the schematic model in Fig. 6(c) the fully extended butoxy appears to have direct overlapping, this may not happen in the real structure.

The growth of the assembly structure is assumed to be a thermodynamic process and it is well known that the two-dimensional crystallization of molecules is dominated by the equilibrium of steric hindrance and van der Waals interaction. On the other hand, thermodynamic considerations suggest that the area of contacting molecular surface should be made as large as possible[1]. A molecular model shows the four-fold arrangement of CuPcOC8 (Fig. 6(d)). Because the close packing of alkane chains leads to an apparent increase in the contacting number of atoms between CuPcOC8 molecules, this may result in much stronger intermolecular interaction between CuPcOC8s than that for CuPc and CuPcBU8.

As discussed before, the interaction between Pc and C18I molecules is suggested to be mainly van der Waals. A full scale illustration of these results may need quantitative estimation of the interaction between identical molecules as well as that between phthalocyanine and C18I. In addition, the difference of interaction strength of these molecules with the substrate should also be considered. This requires rigorous modeling. Our preliminary calculation did not produce sufficient evidence for interpretation

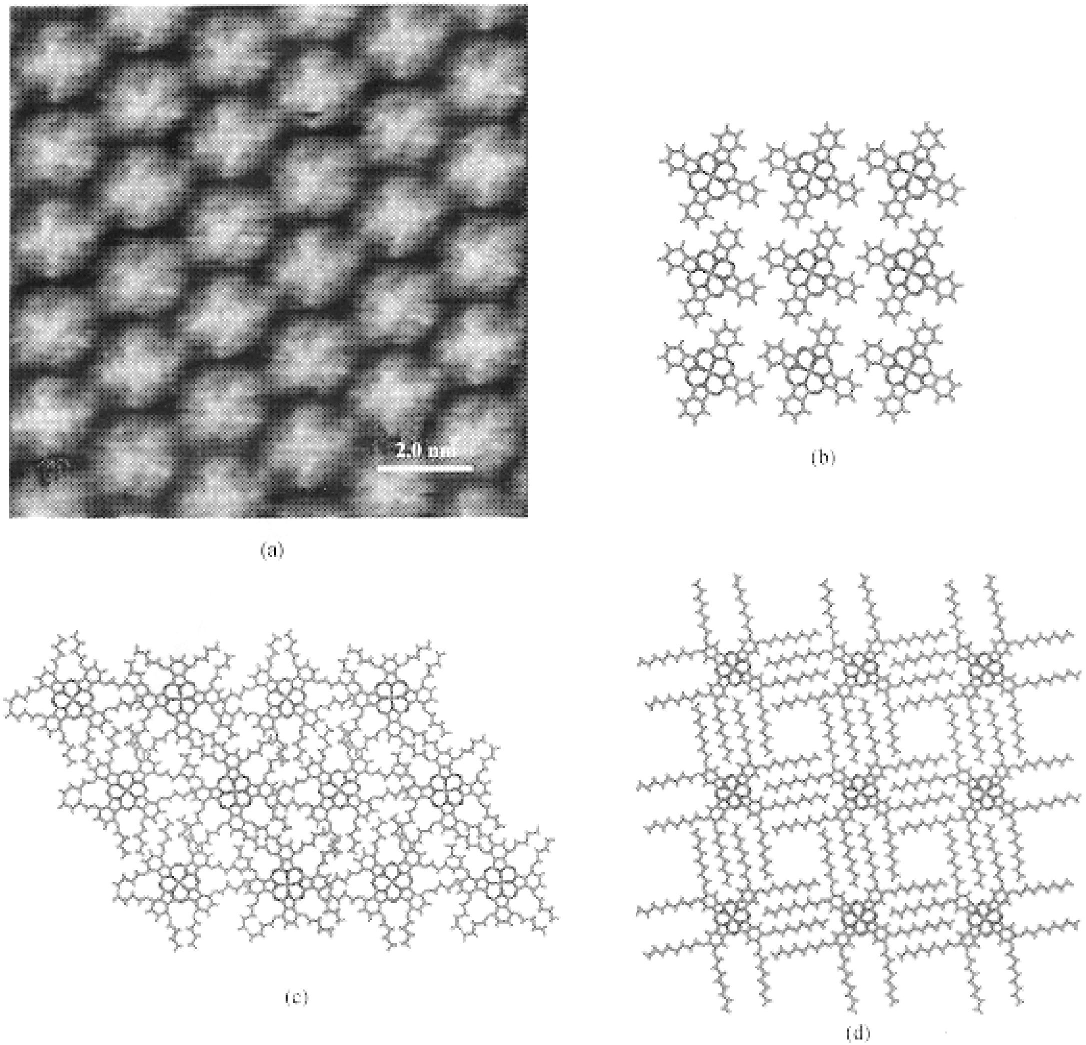

Fig. 6. High-resolution STM images obtained on the two-dimensional domains of closely packed CuPcBU8 (a), and simulated molecular models (b) CuPc, (c) CuPcBU8 and (d) CuPcOC8.

of the assembly and suggested that more rigorous modeling is needed. Besides the systems demonstrated above, the codeposition of CuPc with other alkane derivatives such as *n*-octadecyl mercaptan, 1-bromooctadecane, 1-chlorooctadecane, octadecanol and stearic acid was also studied and homogenous assembly has been found in the case of *n*-octadecyl mercaptan, 1-bromooctadecane, 1-chlorooctadecane, but when coadsorb with octadecanol and stearic acid only phase separation has been found[23,24], thus we consider that the interaction between Pc and the end group of the alkane derivative and the strength of interaction between functional groups of alkane derivatives play an important role in the assembling process. In order to further understand the role of intermolecular interaction in the surface assembling process, more systematical investigations are also undergoing.

3 Conclusion

By altering the substitution groups attached to the phthalocyanine, different assembly behavior with C18I has been observed on the surface of graphite. It is suggested that the observed assembly behavior is associated with the difference of intermolecular interaction between Pc molecules associated with the substitute groups. This work demonstrated that by adjusting the intermolecular interaction, capability of fine control of the assembly behavior can be obtained.

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